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Large thermal conductivity decrease in point defective Bi₂Te₃ bulk materials and superlattices

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Defective Bi_2Te_3 structures have been studied with the aim of lowering the thermal conductivity in order to improve the thermoelectric figure of merit. The cross-plane thermal conductivities of structures containing point defects have been computed by means of molecular dynamics techniques, finding a maximum decrease of 70% for a 4% concentration of tellurium atom vacancies. Superlattices with modified stoichiometries have also been considered in order to find the configuration having the lowest thermal conductivity. In this case, a maximum decrease of 70% was also found. These predictions open the way to the design of efficient bulk thermoelectric materials having optimised thermal properties similar to those of superlattices. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4772783]

I. INTRODUCTION

The interest for high-performance thermoelectric materials has increased in the last decades due to the development of new deposition methods allowing one to tailor the properties of materials through structural engineering at atomic level. The effectiveness of thermoelectric materials is usually quantified by the dimensionless figure of merit *ZT*, defined by $ZT = S^2 \sigma T / \lambda$, where *S* is the Seebeck coefficient, σ is the electrical conductivity, *T* is the temperature, and λ is the sum of the lattice and electronic thermal conductivities. Recent efforts in increasing the *ZT* value were mainly made by trying to decrease the thermal conductivity, the nanostructuration being the key to achieve this task.^{1–3}

At room temperature, Bi_2Te_3 is the best thermoelectric material with a figure of merit near to unity. It belongs to the classic thermoelectric materials that have a large Seebeck coefficient.⁴ The origin of this property is its significant anisotropy, which is due to the difference in strength between the weak Van der Waals bonds connecting adjacent Te atoms and the strong covalent bonds between the Bi and Te atoms.⁵ As a consequence, Bi_2Te_3 has a lattice thermal conductivity similar to that of amorphous materials.

Owing to its good thermoelectric figure of merit at room temperature, bismuth telluride and some related ternary alloys are often used for cooling applications based on the Peltier effect or for power generation based on the Seebeck effect. Porous bismuth telluride, thin films,^{3,6} nanowires, or nano-tubes exhibit lower thermal conductivity^{7,8} than bulk Bi₂Te₃. Incorporation of dopants like antimony or selenium,⁹ changes

of stoichiometry and intentional introduction of structural defects, are some ways to decrease its thermal conductivity.⁹ Several authors claimed that the natural or artificial nanostructuration of Bi₂Te₃ can lead to a decrease of the thermal conductivity.^{2,10–12} Nanostructuration enhance the phonon scattering at the boundaries or phonon blocking effects due to the low-dimensionality features.^{13,14} The structural modulation at the nanometer scale of Bi₂Te₃ is the object of the present work. We focus on the cross-plane thermal conductivity, as it is the lowest one due to the lamellar structure of Bi₂Te₃.

According to the Slack's principle of "phonon glass and electron crystal,"¹⁵ new generation thermoelectric materials should conduct electricity as well as crystalline conductors, and conduct heat as badly as glasses. From a structural point of view, ideal thermoelectric materials should contain (1) long-periodic -with heavy elements as the best-lattice structures, and (2) ordered/disordered pores and other defect systems, like superlattices^{16–18} and thin films of different structures and compositions to enhance the scattering of thermal phonons.¹⁹ The lattice thermal conductivity, which is predominant for semiconducting materials, strongly depends on the presence of additional sources of phonon scattering. This scattering can be increased by reducing the phonon mean free path by the introduction of lattice alloy disorder, vacancies or substitution defects, or even decreasing the dimensionality of the lattice as in thin films or in nanowires. The large temperature fluctuations of the usual thermoelectric devices are an additional reason for a deep investigation of the thermal and mechanical properties of these materials.²⁰

The paper is organized as follows. Section II provides a short description of the numerical method that we have used for the simulation of the thermal conductivity, i.e., the non-

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equilibrium molecular dynamics (NEMD) as well as of the systems that we have considered. Section III addresses the lattice thermal conductivity of Bi₂Te₃ with vacancies and antisite defects. We also consider superlattices built with the compounds having the stoichiometries, which provide the most interesting properties. In Sec. IV, our conclusions are summarized.

II. METHODS, SYSTEMS, AND TESTS

A. Computational method

Molecular dynamics is usually implemented according the two main methodologies, i.e., equilibrium molecular dynamics (EMD) and NEMD. Among the various nanoscale simulation approaches, these two methods are often the preferred ones, because they do not require the knowledge of the relaxation time of phonons, as it is the case when solving the Boltzmann transport equation or when performing Monte Carlo calculations.

In the present paper, the Bi₂Te₃ lattice thermal conductivity is evaluated by means of the NEMD method,^{21,22} which is also known as the direct method, and is similar to the hot-plate/cold-plate experimental setup proposed by Kotake and Wakuri.^{23,24} As it is shown by a plethora of examples, NEMD is often the method of choice for the investigation of nanostructures, while EMD is sometimes preferred for studying the bulk thermal conductivity.

In our NEMD simulations, the heat flux is generated along the z direction perpendicular to the planes involving the same atoms and periodic boundary conditions in all the three directions are applied. We only predict the cross-plane thermal conductivity as it is the direction with the lower thermal conductivity. The planar heat source and heat sink are located at $\frac{1}{4}$ and $\frac{3}{4}$ of the simulation cell. Owing to the assumption of periodic boundary conditions, the resulting steady state temperature profile is symmetric with respect to the positions of the two thermostats that are set perpendicularly to the z-direction. After reaching the steady state obtained after 1×10^6 of time steps, the temperature profile and the heat power of the two thermostats are collected over 5 to 10×10^6 of time steps depending on the system size, in order to achieve a good statistical accuracy.^{25,26} The time-step is set equal to 0.001 ps. Then, the thermal conductivity is determined using the Fourier's law. This method has been widely used for the study of heat transfer at nanoscales.^{16,17,26–29} The EMD method has also been employed with success,^{17,30} but a comparative analysis is not in the scope of this article.

In all the calculations, we have used the two-body interatomic Morse potential developed by Qiu and Ruan.³¹ This potential reproduces the elastic properties and the phonon dispersion data quite accurately, which is an essential prerequisite for the correct description of the thermal properties. It is a two-body potential $\varphi(r_{ij})$ containing two terms, i.e., a short-range interaction term $\varphi_{SR}(r_{ij})$ and a Coulombic term describing the long-range electrostatic interactions. Its expression is given by

$$\varphi(r_{ij}) = \varphi_{SR}(r_{ij}) + \frac{q_i q_j}{r_{ij}}$$

where q_i and q_j are the effective ionic charges and r_{ij} is the distance between the atoms *i* and *j*. The short-range contribution reads

$$\varphi_{SR}(r_{ij}) = D_e[\{1 - e^{-\alpha(r_{ij} - r_0)}\}^2 - 1],$$

where D_e is the depth of the potential well, r_0 is the equilibrium distance, and α is related to the bond elasticity.³¹ Alternatively, we could have used another potential recently developed by Huang and Kaviany,³² but their three-body potential has a quite complicated expression and does not provide results that are much more accurate than those obtained by the Qiu and Ruan two-body potential.³¹ Other Bi₂Te₃ potentials exist in the literature, but they are not appropriate for lattice thermal conductivity calculations because they do not include anharmonic effects.^{33,34}

The effective charges are assumed to be -0.26 for Te₁, 0.38 for Bi, and -0.24 for Te₂, while the masses are 127.6 amu and 208.9804 amu for Te and Bi, respectively. The long-range Coulombic interactions are computed by performing the Ewald's summation. The cut-off is set to 30.0 Å for the Morse potential and to 11.0 Å for the Coulombic interactions. These latter values were taken from the Qiu and Ruan paper.³¹ Finally, the average temperature of the system was kept constant in all simulations, while the thermostats are set to a temperature difference of 10% with respect to the average temperature of the system.

B. Bi₂Te₃ and related structures

Bismuth telluride has a tetradymite crystal structure, with the space group D_5^{3d} and the point group $R\bar{3}m$.^{33,35} The hexagonal cell parameters are a = b = 4.386 Å and c = 30.497 Å. The unit cell contains 15 atoms, i.e., 3 quintuples. Each quintuple has two nonequivalent Te atoms and its atoms are arranged in planes perpendicular to the c-axis according to the sequence $-Te_1 - Bi - Te_2 - Bi - Te_1 -$. This sequence is periodically repeated in the direction of c. The Te₁ atoms at the edges of the quintuple form ionic bonds with *Bi*, while the bonds between two Te₁ atoms belonging to different quintuples are a mixture of Van der Waals and covalent interactions. These latter bonds are thus weaker than the former ones.

For bulk Bi₂Te₃ and for superlattices, we have used simulation cells having the following sizes: $8 \times 8 \times 2$, $8 \times 8 \times 4$, and $8 \times 8 \times 8$ units cells, i.e., 1920, 3840, and 7680 atoms, respectively. The Bi₂Te₃ cell projected on the yz-plane is shown in Figure 1. For the bulk Bi₂Te₃ and the superlattices, the thermal conductivities of the infinite size systems were determined by the method proposed by Schelling,³⁶ which consists in extrapolating the inverse thermal conductivity versus the inverse system size in the z direction. In Figure 2, the reciprocal of the bulk Bi₂Te₃ thermal conductivity is reported as a function of the reciprocal of the system size. Actually, LAMMPS calculations were performed in "k-space style: ewald/n," a feature that limits to about 10 000 the number of atoms taken into account in the simulation. Nevertheless, it can be seen in Figure 2 that results for just three system sizes allow one to be confident about the



FIG. 1. Bi_2Te_3 structure in the *yz*-plane with quintuples and the hexagonal conventional cell structure. Each quintuple has five monolayers in the sequence: Te-type1, Bi, Te-type2, Bi, Te-type1. Three quintuples form the hexagonal conventional cell structure.

accuracy of a linear extrapolation to an infinite size (correlation coefficient $R \ge 0.998$).

For the computation of the defective Bi_2Te_3 effective thermal conductivity, only a simulation cell of size $8 \times 8 \times 4$ was used. Actually, for these latter systems, we were mainly interested in evaluating the influence of the presence of vacancies and antisite defects on the thermal conductivity in comparison to the thermal conductivity of the bulk Bi_2Te_3 of the same size.

C. Test of the simulation approach: Bulk Bi₂Te₃

The thermal conductivity of the infinite size bulk Bi_2Te_3 is plotted in Figure 3 as a function of the temperature. In the same figure, Qui *et al.* EMD results, obtained using the same interatomic potential that we have used, are also reported. The comparison is also performed with the results of a Debye-Callaway (DC) model^{37,38} and with the experimental data reported in three papers.^{39–41} At room temperature, the three experimental values are 1.57 W/mK by Goldsmid,³⁹ 1.70 W/mK by Satterthwaire-Ure⁴⁰ and 0.88 W/mK by Kaibe *et al.*⁴¹ The NEMD method yields a thermal conductivity in very close agreement with the first two experimental values. The thermal conductivity obtained by the EMD method is lower than the one given by NEMD. This behavior has been



FIG. 2. Reciprocal of the thermal conductivity versus reciprocal of the system size for bulk Bi_2Te_3 at 300 K.



FIG. 3. Bulk Bi₂Te₃ thermal conductivity, calculated by NEMD and extrapolated to infinite size, as a function of the temperature (black squares). Theoretical results obtained with EMD by Qiu and Ruan³¹ and three sets of experimental results are also plotted for comparison (exp1,³⁹ exp2,⁴⁰ and exp3 (Ref. 41)). The discrepancies between the experimental results might be due to the quality of the samples' atomic structure.

observed in several systems^{17,42,43} and is related to the description of phonons at the equilibrium (EMD) or out-of-equilibrium (NEMD) regimes.

The thermal conductivity of bulk Bi_2Te_3 shows a temperature dependence typical of crystalline solids. At higher temperatures, the phonon-phonon scattering is the predominant scattering process and yields a 1/T dependence. This reduction of the thermal conductivity with the temperature within the Debye model is explained by the increased Umklapp scattering rate. Higher temperatures involve a greater number of phonons, which, in turn, gives rise to a higher scattering probability.

III. RESULTS

Depending on the deposition method, Bi_2Te_3 can be found with different stoichiometries. Excess of *Bi* atoms are accommodated in single crystalline Bi_2Te_3 to the three point defect mechanisms: antisite defects, additional regular *Bi* sites, or substitution defects and interstitial *Bi* atoms. The two first kinds of defects² are investigated here. Cho *et al.*⁴⁴ have grown thin films with an excess of Te, and this excess was explained by the presence of antisite defects, in which Te atoms occupied Bi lattice sites. Using stochastic procedures, we have excluded Bi or Te atoms and generated stoichiometries with a vacancy concentration varying from 1% to 10%. We have also interchanged Bi and Te atoms to create antisite or antistructural defects.⁴⁵ In all cases, the defects are introduced in the lattice in a totally random fashion and are desultory.

In this section, the thermal conductivities calculated by NEMD are presented for both vacancy and antisite defects. For the defected systems, only $8 \times 8 \times 4$ structures were used to compute an effective thermal conductivity. The interest here is to estimate the change of the bismuth telluride thermal conductivity induced by the presence of vacancies or other defects. Afterwards, we will also consider bismuth

TABLE I. Structures studied for the vacancy defects.

Percentage	n-type	p-type
1	Bi ₃₉ Te ₆₀	Bi ₄₀ Te ₅₉
2	Bi ₃₈ Te ₆₀	Bi ₄₀ Te ₅₈
3	Bi ₃₇ Te ₆₀	Bi ₄₀ Te ₅₇
4	Bi ₃₆ Te ₆₀	Bi ₄₀ Te ₅₆
5	Bi ₃₅ Te ₆₀	Bi ₄₀ Te ₅₅
6	Bi ₃₄ Te ₆₀	Bi ₄₀ Te ₅₄
7	Bi ₃₃ Te ₆₀	Bi ₄₀ Te ₅₃
8	Bi ₃₂ Te ₆₀	Bi ₄₀ Te ₅₂
9	Bi ₃₁ Te ₆₀	Bi ₄₀ Te ₅₁
10	Bi ₃₀ Te ₆₀	Bi ₄₀ Te ₅₀

telluride superlattices composed of the structures, which exhibit the lowest thermal conductivity.

A. Vacancy defects

Several stoichiometries (see Table I) of monocrystalline $Bi_{40-x}Te_{60}$ (x = 1 to 10) and $Bi_{40}Te_{60-y}$ (y = 1 to 10), which are n-type and p-type semiconductors, respectively, have been studied. An example of structure with 3% of Bi vacancies, is shown in Figure 4. Structures with concentrations of Te vacancies greater than 7% were found to be unstable. The purpose of the present study is to find the stoichiometries yielding the lowest thermal conductivity and potentially the highest ZT value.

The thermal conductivity of bismuth telluride decreases both in the presence of Bi or Te vacancies. The decrease is greater than 60% when the bismuth vacancy concentration is 5% and it is greater than 70% for a tellurium vacancy concentration of 4% (as reported in Figure 5). It is interesting to note that in both cases there is an optimum vacancy concentration to attain the minimum thermal conductivity. Actually, the vacancies destroy the continuity of the lattice and constitute an additional scattering mechanism for phonons. The significant reduction of the thermal conductivity is very promising in view of a further increase of the thermoelectric figure of merit.



FIG. 4. Example of vacancy defected structure, with Bi vacancies $Bi_{37}Te_{60}$. The red squares with the white filling represent the vacances.



FIG. 5. Calculated thermal conductivity for defected bulk Bi_2Te_3 obtained from NEMD for a system size of $8 \times 8 \times 4$ cells as a function of the vacancy defect percentage. Left side of the figure corresponds to $Bi_{40-x}Te_{60}$ and right side to $Bi_{40}Te_{60-y}$.

Finally, we mention that we have not taken into account the effects due to the presence of the additional charge carriers introduced by the defects. These additional charges give two opposite contributions to the thermal conductivity: on one hand, they increase it, because they contribute to the heat conduction on the other hand, they provide an additional scattering mechanisms for the phonons, which gives rise to a decrease in thermal conductivity. In our study, we only consider the lattice thermal conductivity, which is the predominant contribution when the semiconductors are not heavily doped.

B. Antisite defects

Several stoichiometries of monocrystalline $Bi_{40-x}Te_{60+x}$ (x = 1 to 10) and $Bi_{40+y}Te_{60-y}$ (y = 1 to 10) were generated by randomly replacing Bi with Te in the first case and Te₁ or Te₂ with Bi in the second one (see Table II). An example of structure with 4% of Bi antisite defects is shown in Figure 6. Both types of Te atoms are replaced by Bi atoms.

In this case, the thermal conductivity for both Bi and Te antisite or substitutional defected structures decreases in comparison with the thermal conductivity of stoichiometric

TABLE II. Stoichiometries studied for the antisite defects.

Percentage	n-type	p-type	
1	Bi ₃₉ Te ₆₁	Bi ₄₁ Te ₅₉	
2	Bi ₃₈ Te ₆₂	Bi ₄₂ Te ₅₈	
3	Bi ₃₇ Te ₆₃	Bi ₄₃ Te ₅₇	
4	Bi ₃₆ Te ₆₄	Bi ₄₄ Te ₅₆	
5	Bi ₃₅ Te ₆₅	Bi45Te55	
6	Bi ₃₄ Te ₆₆	Bi ₄₆ Te ₅₄	
7	Bi ₃₃ Te ₆₇	Bi ₄₇ Te ₅₃	
8	Bi ₃₂ Te ₆₈	Bi48Te52	
9	Bi ₃₁ Te ₆₉	Bi49Te51	
10	Bi ₃₀ Te ₇₀	Bi ₅₀ Te ₅₀	



FIG. 6. Example of defected antisite structures. The red squares represent Te atoms that replace Bi atoms, while the green squares represent Bi atoms that occupy Te type-1 and Te type-2 atomic positions.

Bi₂Te₃, but the decrease is much smaller than in the vacancies case. This was expected as the antisite defects disturb less the overall structure. At the case of vacancy defects, the modification of the coordination number effects the lattice vibrations. The atomic movements close to an antisite defect is much less perturbated compared to the vacancy defect. With the exception of $Bi_{41}Te_{59}$, where the reduction is on the order of 40%, all the other stoichiometries have almost the same behavior, with a thermal conductivity reduction of 20% (as illustrated in Figure 7).

C. Superlattices

Enhanced ZT values in thermoelectric materials can be obtained by the periodic inclusion of quantum dots in bulk materials or using phonon-blocking/electron-transmitting superlattices in the thin-film form.¹³ In the last few decades, research in this direction has given excellent results, in





0.7

0,6

0,5

0,4

0,3

Thermal Conductivity (W/m²K) 0,2 0,1 0.0 3010 2010 2010 8010 2010 2010 3010 2010 5010 5010 Antisite percentage

FIG. 7. Calculated thermal conductivity for defected bulk Bi2Te3 obtained by NEMD for a system size of $8 \times 8 \times 4$ cells as a function of the antisite defect percentage. The left side of the figure corresponds to $Bi_{40-x}Te_{60+x}$ and the right side to $Bi_{40+x}Te_{60-x}$.

particular, in the case of Bi₂Te₃/Sb₂Te₃ superlattices, for which a ZT = 2.4 (Refs. 1, 46, and 47) value was found. This important enhancement of the figure of merit is due to the changes induced by superlattices on the transport phonon properties.

As the vacancy defected structures exhibit an important reduction of thermal conductivity, we have considered three types of pseudo-superlattices: Bi₃₅Te₆₀/Bi₄₀Te₆₀, Bi₄₀Te₅₆/ $Bi_{40}Te_{60}$, and $Bi_{35}Te_{60}/Bi_{40}Te_{56}$, with two periods for each. These pseudo-superlattices have a particular distribution of defects. In Figure 8, a schematic representation of the three types of superlattices is given that includes three and six quintuples as half period. The choice of these two periodicities is justified by the fact that superlattices of $Bi_2Te_3/$ Sb₂Te₃ have the lowest thermal conductivities for periodicities of 1 to 3 nm.46,47

BiasTean 3 quintuples Bi₄₀Te₅₆ 3 quintuples

SL: (Bi35Te60)2/(Bi40Te56)2



FIG. 9. Calculated thermal conductivity for the bulk infinite size Bi_2Te_3 and for superlattices with modified stoichiometries. The 1/1 and 2/2 show the number of quintuples per semiperiods, e.g., the 1/1 label means that 3+3 quintuples of the two materials composing the superlattice period are involved.

The thermal conductivity of defected/non-defected and defected/defected pseudo-superlattices is considerably smaller than the corresponding value of the non-defected Bi_2Te_3 (Figure 9), but the decrease is not as large as could be expected. For the $Bi_{40}Te_{60}/Bi_{35}Te_{60}$ superlattice, the reduction is about 60%, and for $Bi_{40}Te_{60}/Bi_{40}Te_{56}$ is 70%, i.e., almost the same reduction as in the case of the $Bi_{35}Te_{60}$ and Bi₄₀Te₅₆ structures, respectively. For these two types of pseudo-super-lattices, the global defects concentration is decreased by half, while the impact on the thermal conductivity remains unchanged. This seems to prove that phonon blocking occurs on a three quintet length only, as the same thermal conductivity decrease is obtained for a homogeneous distribution of defects. Pernot et al. showed that a few number of quantum dot layers allows blocking 90% of the thermal phonons in Si.⁴⁸ The third type of superlattices, i.e., Bi₃₅Te₆₀/Bi₄₀Te₅₆ exhibits thermal conductivity reduction of 75%. The fact that the conjugation of two different types of defects yields an even stronger decay shows that each type of defected layer blocks different range of phonons. Furthermore, we have found that the effect of the periodicity on the thermal conductivity is quite small and this can be explained to the correlation of the phonon mean free path to the pseudo-superlattice period. The mean free path is lower than the periodicity.

IV. CONCLUSION

Non-equilibrium molecular dynamics simulations have been performed with the aim of calculating the thermal conductivity of bulk and structurally modulated Bi_2Te_3 . After validating of the method in the case of the bulk material by comparing our results to experimental data and other theoretical results, we have studied the effect of the presence of vacancies and antisite defects on the thermal conductivity. The vacancies reduce the thermal conductivity more than the antisite defects. This was expected, because an antisite defect consists of the exchange of a pair of atoms, which is a smaller perturbation of the lattice periodicity than a vacancy, which affects the continuity of the lattice. Chiritescu *et al.*³⁷ studied the lower limit of the thermal conductivity of nanostructured Bi_2Te_3 -based materials and showed that this lower limit is 0.31 W/mK in the case of grained pure Bi_2Te_3 . Extrapolating our results for the stoichiometry yielding the lowest thermal conductivity for the bulk system to the infinite size system, we find a value of 0.45 W/mK for the configuration of vacancy defected Bi_2Te_3 .

The present theoretical study shows that an important reduction of the Bi_2Te_3 thermal conductivity can be obtained by introducing point defects into the lattice. The thermal conductivity can be decreased down to 70% by a small amount of tellurium atom vacancies. Superlattices based on the defected Bi_2Te_3 structures that exhibit the lowest thermal conductivities do not seem to be very promising. Randomness is increased with the $Bi_{35}Te_{60}/Bi_{40}Te_{56}$ configuration compared to the bulk case and the subsequent thermal conductivity decrease is indeed larger. $Bi_{40}Te_{60}/Bi_{40}Te_{56}$ and $Bi_{40}Te_{60}/Bi_{35}Te_{60}$ SLs yield thermal conductivity decrease similar to the ones of the bulk case. Due to the independence to period, we presume that the complete phonon blocking process due to vacancies occurs within three quintuples.

The expected significant reduction of the thermal conductivity due to phonon confinement and interfacial scattering was not found. Considering Bi_2Te_3/Sb_2Te_3 superlattices with defected Bi_2Te_3 compounds could be a way of obtaining materials with lower thermal conductivity values than the one predicted for the bulk limit, i.e., 0.22 W/mK as reported in the literature.⁴⁷ These findings can be used as a guideline for synthesizing optimal thermoelectric bismuth telluride materials.

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